US 20150236324A1

(19) **United States**

(12) **Patent Application Publication**

Xiao et al.

(10) **Pub. No.: US 2015/0236324 A1**

(43) **Pub. Date: Aug. 20, 2015**

(54) LITHIUM-BASED BATTERY SEPARATOR AND METHOD FOR MAKING THE SAME

(71) Applicant: **GM GLOBAL TECHNOLOGY OPERATIONS LLC**, Detroit, MI (US)

(72) Inventors: **Qiangfeng Xiao**, Troy, MI (US); **Anne M. Dailly**, West Bloomfield, MI (US); **Li Yang**, Troy, MI (US); **Zhongyi Liu**, Troy, MI (US); **Mei Cai**, Bloomfield Hills, MI (US)

(21) Appl. No.: **14/617,322**

(22) Filed: **Feb. 9, 2015**

Related U.S. Application Data

(60) Provisional application No. 61/941,054, filed on Feb. 18, 2014.

Publication Classification

(51) **Int. Cl.**

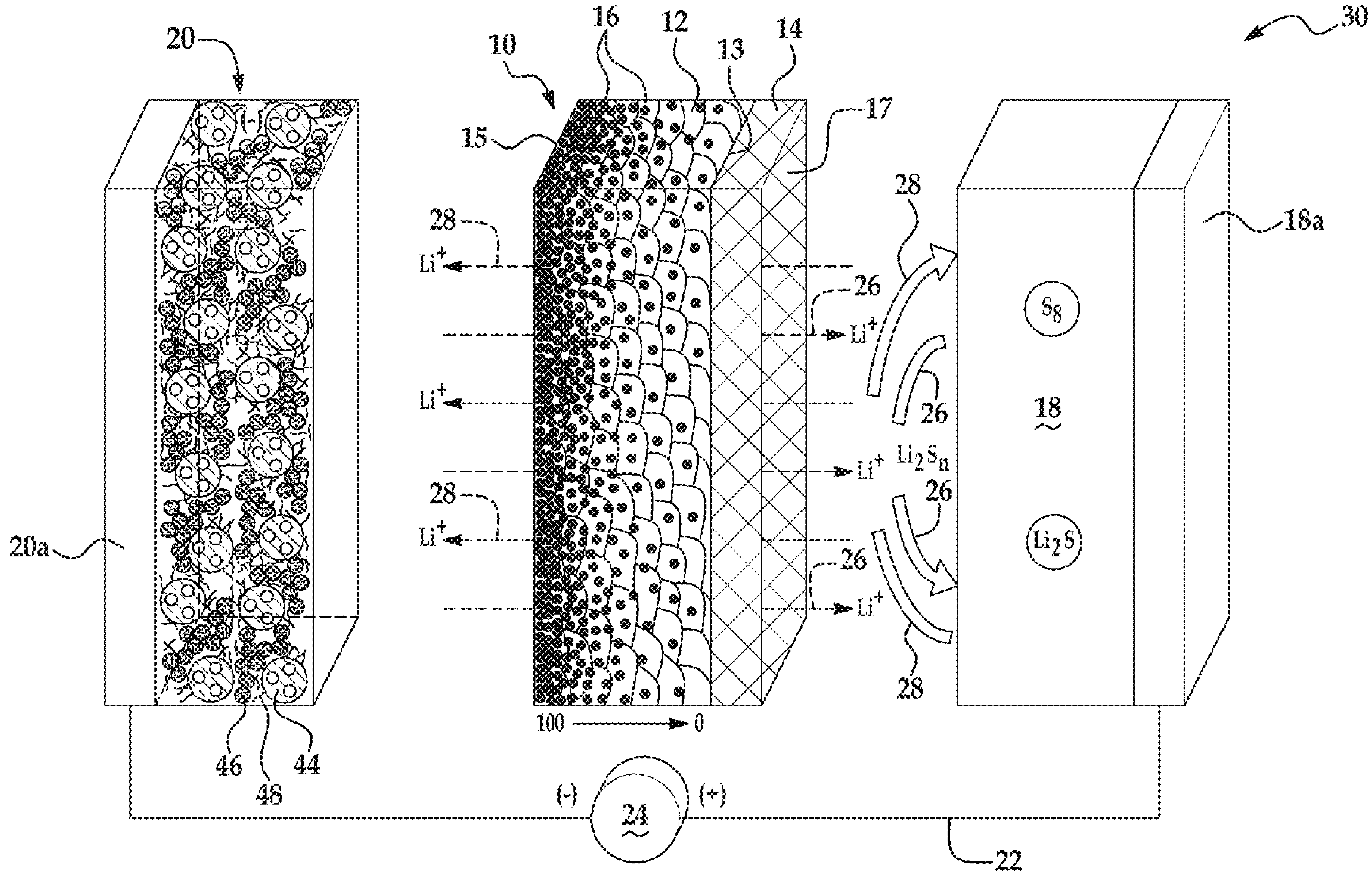
H01M 2/16	(2006.01)
H01M 2/14	(2006.01)
H01M 10/052	(2006.01)

(52) **U.S. Cl.**

CPC ***H01M 2/1686*** (2013.01); ***H01M 10/052*** (2013.01); ***H01M 2/145*** (2013.01); *H01M 2220/10* (2013.01); *H01M 2220/30* (2013.01); *H01M 2220/20* (2013.01)

(57) ABSTRACT

A lithium-based battery separator includes a porous polymer membrane having opposed surfaces. A porous carbon coating is formed on one of the opposed surfaces of the porous polymer membrane. Polycations are incorporated in the porous carbon coating, in the porous polymer membrane, or in both the porous carbon coating and the porous polymer membrane.



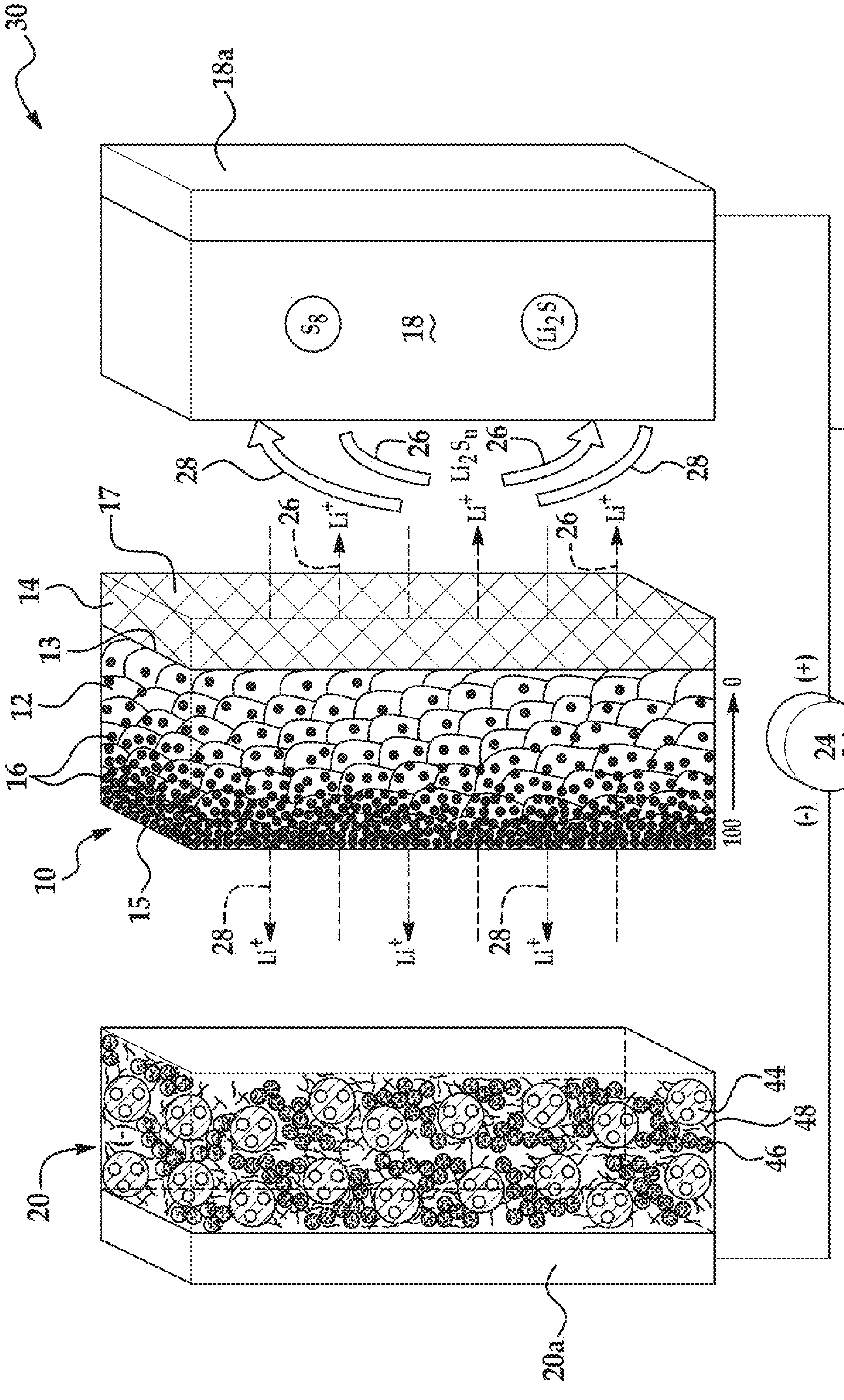

30
18a
S_8
18
Li_2S
22
26
26
28
28
Li_2S_n
Li^+
Li^+
Li^+
17
14
13
12
16
10
15
100
0
24
(-)
(+)
28
28
Li^+
Li^+
Li^+
20
20a
44
48
46

FIG. 1

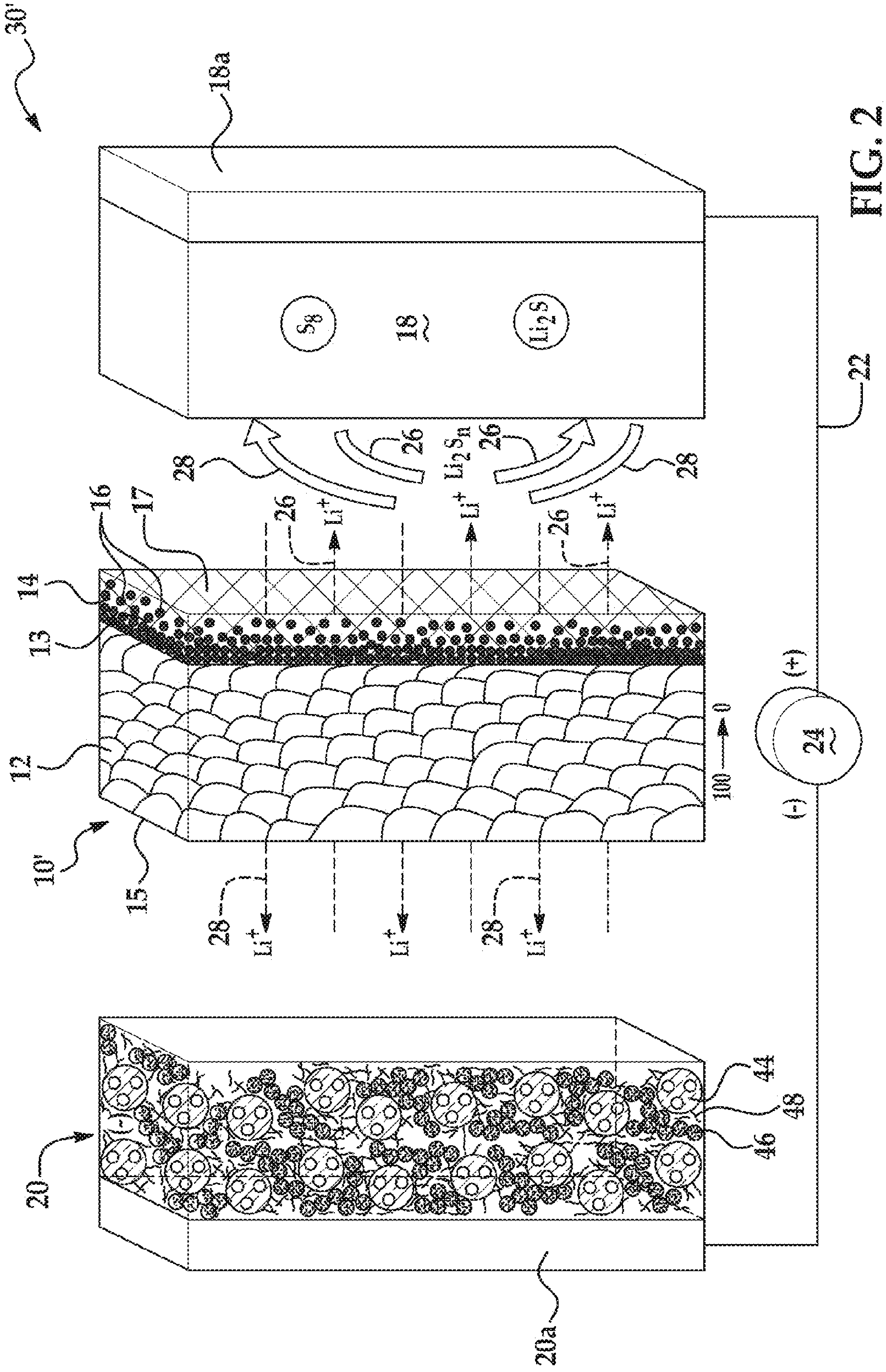

30'
18a
18
S_8
Li_2S
22
28
26
Li_2S_n
26
28
16
17
14
13
12
10'
15
26
Li^+
Li^+
26
Li^+
28
Li^+
Li^+
28
Li^+
100 → 0
(-)
24
(+)
20
(-)
20a
44
48
46

FIG. 2

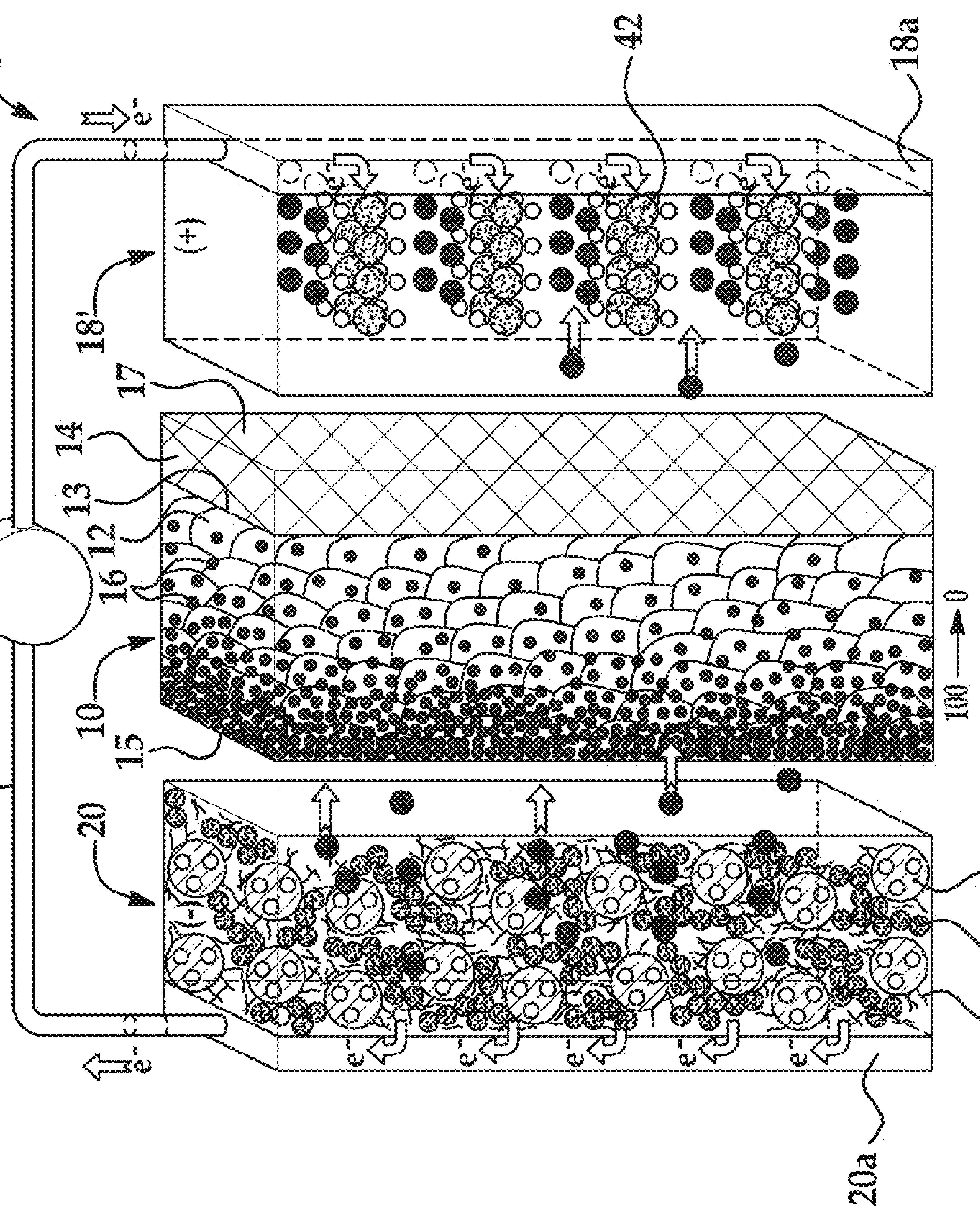


FIG. 3

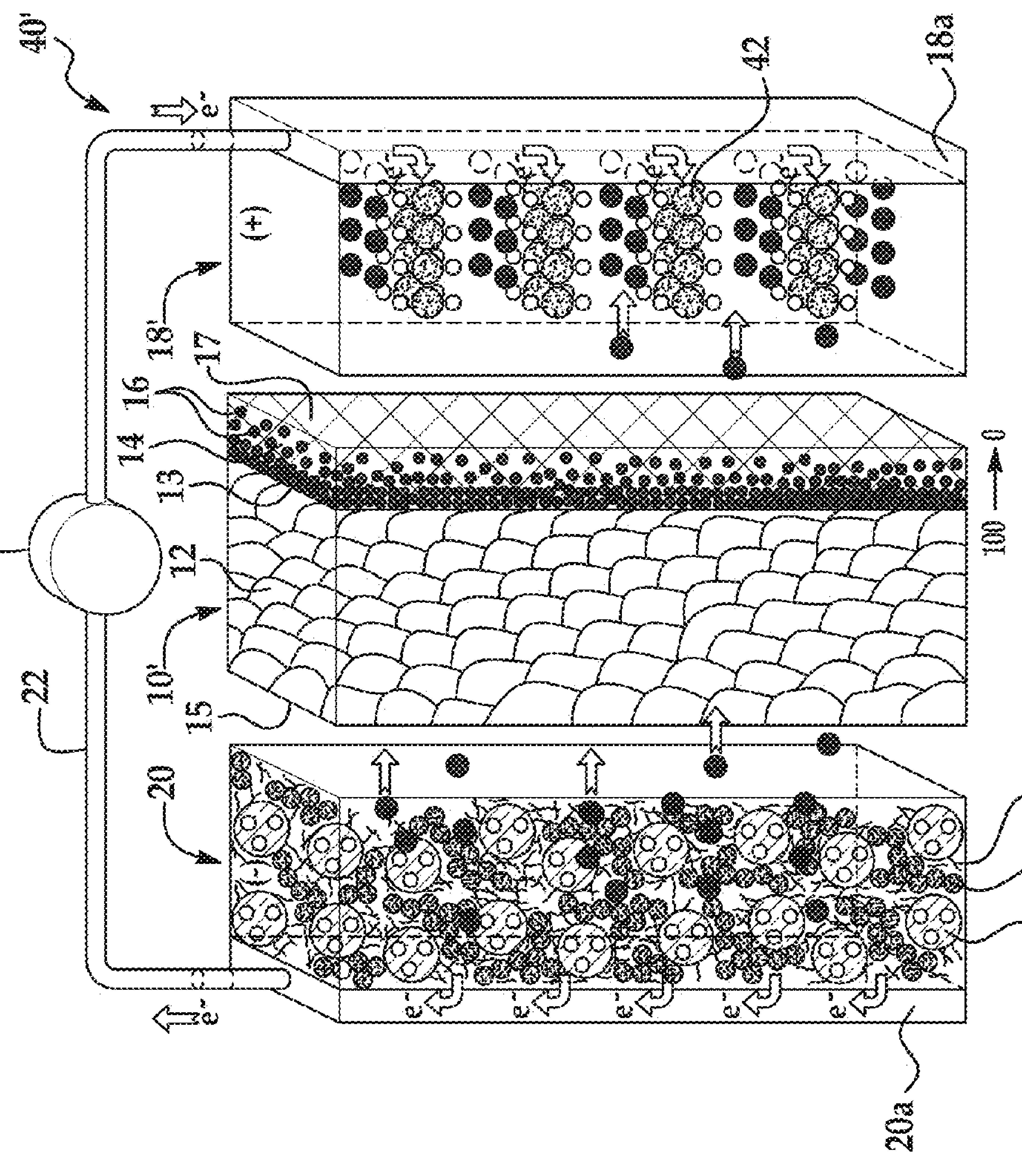
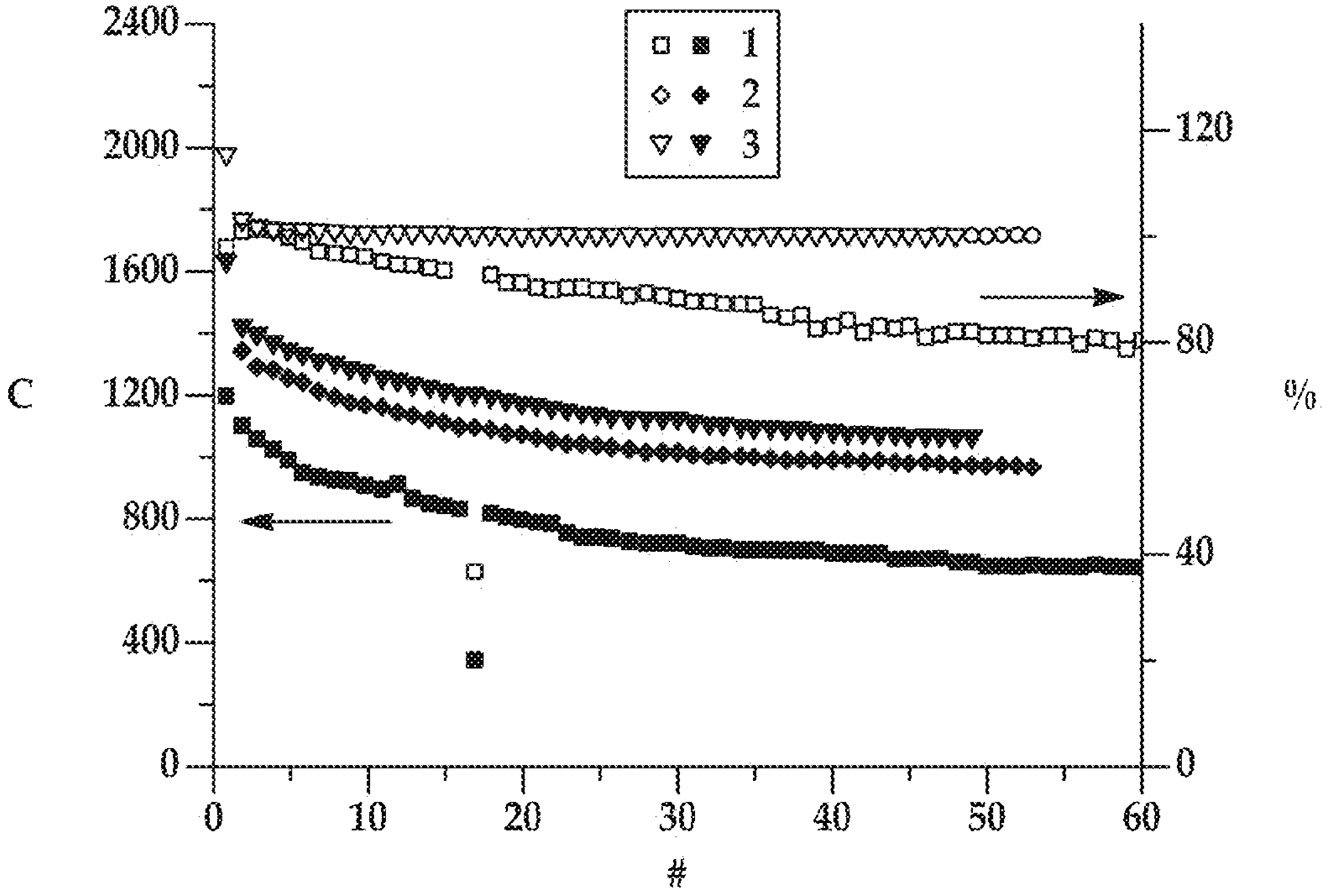
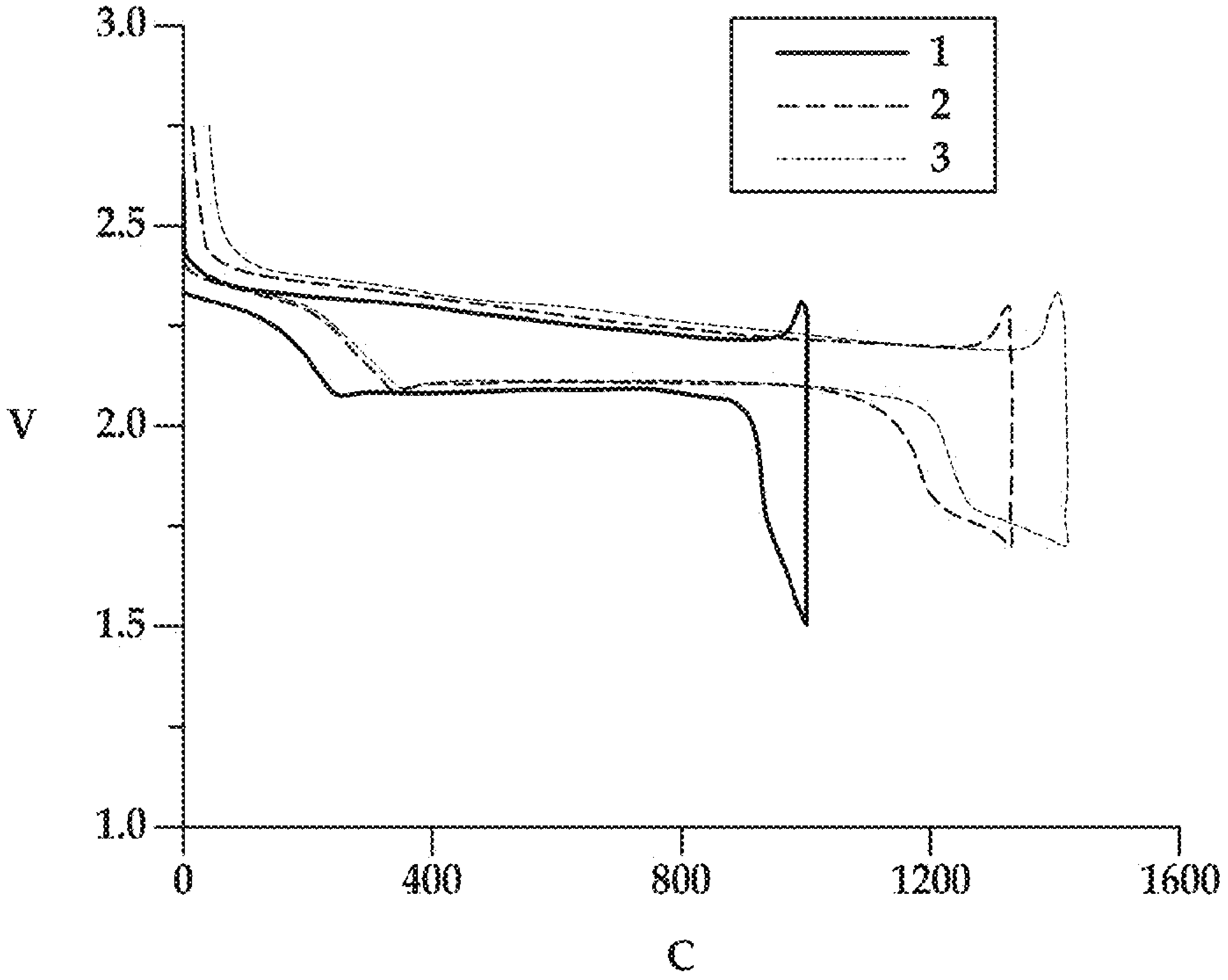


FIG. 4



□ ■ 1
◇ ◆ 2
▽ ▼ 3
2400
2000
1600
1200
800
400
0
C
120
80
40
0
%
0
10
20
30
40
50
60
#

FIG. 5



1
2
3
3.0
2.5
2.0
1.5
1.0
V
0
400
800
1200
1600
C

FIG. 6

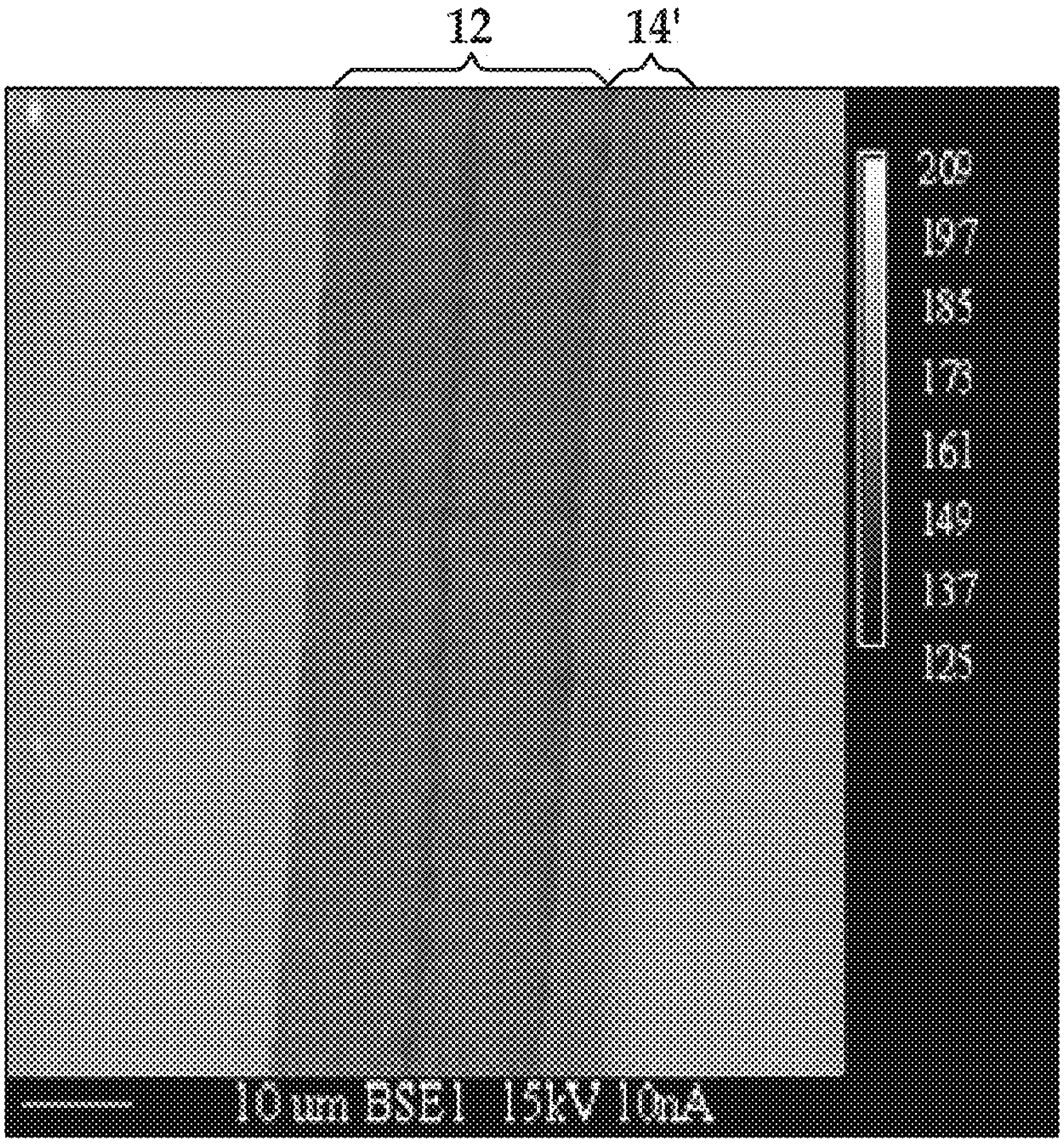

12
14'
209
197
185
173
161
149
137
125
10 um BSE1 15kV 10nA

FIG. 7A

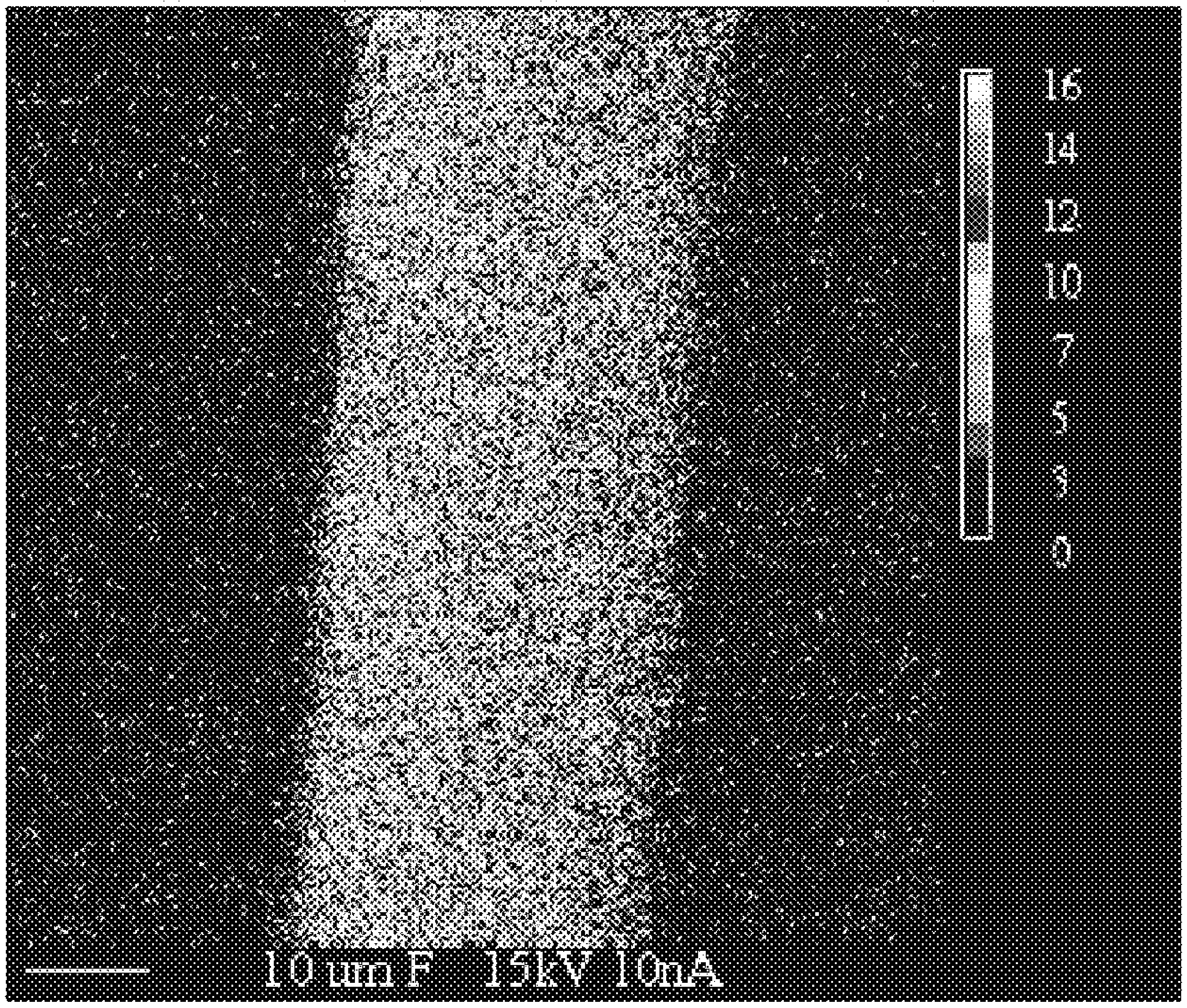

16
14
12
10
7
5
3
0
10 um F 15kV 10nA

FIG. 7B

LITHIUM-BASED BATTERY SEPARATOR AND METHOD FOR MAKING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application Ser. No. 61/941,054, filed Feb. 18, 2014, which is incorporated by reference herein in its entirety.

BACKGROUND

[0002] Secondary, or rechargeable, lithium-sulfur batteries or lithium ion batteries are often used in many stationary and portable devices, such as those encountered in the consumer electronic, automobile, and aerospace industries. The lithium class of batteries has gained popularity for various reasons including a relatively high energy density, a general nonappearance of any memory effect when compared to other kinds of rechargeable batteries, a relatively low internal resistance, and a low self-discharge rate when not in use. The ability of lithium batteries to undergo repeated power cycling over their useful lifetimes makes them an attractive and dependable power source.

SUMMARY

[0003] A lithium-based battery separator includes a porous polymer membrane having opposed surfaces. A porous carbon coating is formed on one of the opposed surfaces of the porous polymer membrane. Polycations are incorporated in the porous carbon coating, in the porous polymer membrane, or in both the porous carbon coating and the porous polymer membrane.

[0004] Examples of the lithium-based battery separator disclosed herein may be included in a separator for a lithium ion battery or a lithium-sulfur battery.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] Features and advantages of examples of the present disclosure will become apparent by reference to the following detailed description and drawings, in which like reference numerals correspond to similar, though perhaps not identical, components. For the sake of brevity, reference numerals or features having a previously described function may or may not be described in connection with other drawings in which they appear.

[0006] FIG. **1** is a schematic, perspective view of one example of a lithium-sulfur battery showing a charging and discharging state, the battery including one example of the separator according to the present disclosure;

[0007] FIG. **2** is a schematic, perspective view of another example of the lithium-sulfur battery showing a charging and discharging state, the battery including another example of the separator according to the present disclosure;

[0008] FIG. **3** is a schematic, perspective view of one example of a lithium ion battery showing a discharging state, the battery including one example of the separator according to the present disclosure;

[0009] FIG. **4** is a schematic, perspective view of another example of a lithium ion battery showing a discharging state, the battery including another example of the separator according to the present disclosure;

[0010] FIG. **5** is a graph illustrating the capacity (mAh/g_s, left Y-axis labeled "C") vs. cycle number (X-axis labeled "#") and the Coulombic efficiency (%, right Y-axis labeled "%") vs. cycle number (X-axis labeled "#") for an example lithium-sulfur cell with an example of the lithium-sulfur battery separator disclosed herein, a first comparative lithium-sulfur cell with a first comparative battery separator, and a second comparative lithium-sulfur cell with a second comparative battery separator;

[0011] FIG. **6** is a graph illustrating voltage profiles (voltage (V) vs. capacity (C)) for the example lithium-sulfur cell, the first comparative lithium-sulfur cell, and the second comparative lithium-sulfur cell in the second cycle;

[0012] FIG. **7**A is a backscatter electron image of the second comparative battery separator; and

[0013] FIG. **7**B is a grey scale representation of the elemental mapping of fluorine (F) for the backscatter electron image of FIG. **7**A.

DETAILED DESCRIPTION

[0014] Lithium-sulfur and lithium ion batteries generally operate by reversibly passing lithium ions between a negative electrode (sometimes called an anode) and a sulfur-based or lithium-based positive electrode (sometimes called a cathode). The negative and positive electrodes are situated on opposite sides of a porous polymer separator soaked with an electrolyte solution that is suitable for conducting the lithium ions. Each of the electrodes is also associated with respective current collectors, which are connected by an interruptible external circuit that allows an electric current to pass between the negative and positive electrodes.

[0015] For a lithium-sulfur battery, the life cycle may be limited by the relatively poor conductivity of sulfur, and by the migration, diffusion, or shuttling of lithium-polysulfide intermediates (LiS_x, where x is $2<x<8$) from the sulfur-based positive electrode during the battery discharge process, through the porous polymer separator, to the negative electrode. The lithium-polysulfide intermediates generated at the sulfur-based positive electrode are soluble in the electrolyte, and can migrate to the negative electrode where they react with the negative electrode in a parasitic fashion to generate lower-order lithium-polysulfide intermediates. These lower-order lithium-polysulfide intermediates diffuse back to the cathode and regenerate the higher forms of lithium-polysulfide intermediates. As a result, a shuttle effect takes place. This effect leads to decreased sulfur utilization, self-discharge, poor cycleability, and reduced Coulombic efficiency of the battery. Even a small amount of lithium-polysulfide intermediates forms an insoluble molecule, such as dilithium sulfide (Li_2S), which can permanently bond to the negative electrode. This may lead to parasitic loss of active lithium at the negative electrode, which prevents reversible electrode operation and reduces the useful life of the lithium-sulfur battery.

[0016] In addition, it has been found that lithium ion batteries are deleteriously affected by the dissolution of transition metal cations from the positive electrode, which results in accelerated capacity fading, and thus loss of durability in the battery. The transition metal cations migrate from the positive electrode to the negative electrode of the battery, leading to its "poisoning". In one example, a graphite electrode is poisoned by Mn^{+2}, Mn^{+3}, or Mn^{+4} cations that dissolve from spinel $Li_xMn_2O_4$ of the positive electrode. For instance, the Mn^{+2} cations may migrate through the battery electrolyte, and deposit onto the graphite electrode. When deposited onto the graphite, the Mn^{+2} cations become Mn metal. It has been shown that a relatively small amount (e.g., 90 ppm) of Mn atoms can poison the graphite electrode and prevent reversible electrode operation, thereby reducing the useful life of the battery. The deleterious effect of the Mn deposited at the negative electrode is significantly enhanced during battery exposure to above-ambient temperatures (>40° C.), irrespective of whether the exposure occurs through mere storage (i.e., simple stand at open circuit voltage in some state of charge) or during battery operation (i.e., during charge, during discharge, or during charge-discharge cycling).

[0017] The shuttling of lithium-polysulfide intermediates to the negative electrode in the lithium-sulfur battery or the poisoning of the lithium ion battery by transition metals dissolving from the positive electrode may be reduced or prevented using the battery separator disclosed herein. The examples of the separator include a porous polymer membrane, a porous carbon coating, and a polycation present in the coating and/or in the membrane (where the presence in the membrane depends, at least in part, on the polycation molecular weight). The porous carbon coating may mitigate or prevent the shuttling of lithium-polysulfide intermediates in the lithium-sulfur battery or the migration of transition metal cations in the lithium ion battery by a variety of mechanisms. For one example, the porous carbon coating may absorb the lithium-polysulfide intermediates. For another example, soft acid-soft base interaction may take place between the polycation (i.e., the soft acid) and lithium-polysulfide intermediates (i.e., the soft base). For yet a further example, the polycations may fill at least some of the pores of the membrane and/or coating, thereby further contributing to the mitigation or prevention of the shuttling of the lithium-polysulfide intermediates in the lithium-sulfur battery. In yet a further example, the presence of the polycation present in the coating and/or in the membrane may repel the transition metal cation (s) and thus prevent them from migrating through to the negative electrode. The reduction or the elimination of lithium-polysulfide intermediate migration in the lithium-sulfur battery leads to higher sulfur utilization and enhanced lithium-sulfur battery cycleability and overall performance. Similarly, the reduction or elimination of transition metal cation migration in the lithium ion battery leads to higher graphite, silicon, or other anode material utilization and enhanced lithium ion battery cycleability and overall performance.

[0018] Referring now to FIGS. **1** and **2**, two examples of the lithium-sulfur battery **30**, **30'** are depicted. The examples of the lithium-sulfur battery **30**, **30'** shown, respectively, in FIGS. **1** and **2** include different examples of the lithium-sulfur battery separator **10**, **10'** disclosed herein.

[0019] The separators **10**, **10'** disclosed herein include the porous polymer membrane **12** having two opposed surfaces **13**, **15**, the porous carbon coating **14** formed on one of the opposed surfaces **13**, and the polycation(s) **16** present in the membrane **12** (as shown in FIG. **1**) or in the coating **14** (as shown in FIG. **2**). While not shown, it is to be understood that in still another example, the polycation(s) **16** may be present in both the membrane **12** and the coating **14**.

[0020] The porous polymer membrane **12** may be formed, e.g., from a polyolefin. The polyolefin may be a homopolymer (derived from a single monomer constituent) or a heteropolymer (derived from more than one monomer constituent), and may be either linear or branched. If a heteropolymer derived from two monomer constituents is employed, the polyolefin may assume any copolymer chain arrangement including those of a block copolymer or a random copolymer. The same holds true if the polyolefin is a heteropolymer derived from more than two monomer constituents. As examples, the polyolefin may be polyethylene (PE), polypropylene (PP), a blend of PE and PP, or multi-layered structured porous films of PE and/or PP. Commercially available porous polymer membranes **12** include single layer polypropylene membranes, such as CELGARD 2400 and CELGARD 2500 from Celgard, LLC (Charlotte, N.C.). It is to be understood that the porous polymer membrane **12** may be coated or treated, or uncoated or untreated. For example, the porous polymer membrane **12** may or may not include any surfactant treatment thereon.

[0021] In other examples, the porous polymer membrane **12** may be formed from another polymer chosen from polyethylene terephthalate (PET), polyvinylidene fluoride (PVdF), polyamides (Nylons), polyurethanes, polycarbonates, polyesters, polyetheretherketones (PEEK), polyethersulfones (PES), polyimides (PI), polyamide-imides, polyethers, polyoxymethylene (e.g., acetal), polybutylene terephthalate, polyethylenenaphthenate, polybutene, polyolefin copolymers, acrylonitrile-butadiene styrene copolymers (ABS), polystyrene copolymers, polymethylmethacrylate (PMMA), polyvinyl chloride (PVC), polysiloxane polymers (such as polydimethylsiloxane (PDMS)), polybenzimidazole (PBI), polybenzoxazole (PBO), polyphenylenes (e.g., PARMAX™ (Mississippi Polymer Technologies, Inc., Bay Saint Louis, Miss.)), polyarylene ether ketones, polyperfluorocyclobutanes, polytetrafluoroethylene (PTFE), polyvinylidene fluoride copolymers and terpolymers, polyvinylidene chloride, polyvinylfluoride, liquid crystalline polymers (e.g., VECTRAN™ (Hoechst AG, Germany) and ZENITE® (DuPont, Wilmington, Del.)), polyaramides, polyphenylene oxide, and/or combinations thereof. It is believed that another example of a liquid crystalline polymer that may be used for the porous polymer membrane **12** is poly(p-hydroxybenzoic acid). In yet another example, the porous polymer membrane **12** may be chosen from a combination of the polyolefin (such as PE and/or PP) and one or more of the other polymers listed above.

[0022] The porous polymer membrane **12** may be a single layer or may be a multi-layer (e.g., bilayer, trilayer, etc.) laminate fabricated from either a dry or wet process. For example, a single layer of the polyolefin and/or other listed polymer may constitute the entirety of the porous polymer membrane **12**. As another example, however, multiple discrete layers of similar or dissimilar polyolefins and/or polymers may be assembled into the porous polymer membrane **12**. In one example, a discrete layer of one or more of the polymers may be coated on a discrete layer of the polyolefin to form the porous polymer membrane **12**. Further, the polyolefin (and/or other polymer) layer, and any other optional polymer layers, may further be included in the porous polymer membrane **12** as a fibrous layer to help provide the porous polymer membrane **12** with appropriate structural and porosity characteristics. Still other suitable porous polymer membranes **12** include those that have a ceramic layer attached thereto (positioned between the remainder of the membrane **12** and the porous carbon coating **14**), and those that have ceramic filler in the polymer matrix (i.e., an organic-inorganic composite matrix).

[0023] The porous carbon coating **14** is formed on one surface **13** of the porous polymer membrane **12**. As illustrated in both FIGS. **1** and **2**, this surface **13** is the surface **13** or **15**

that faces (or will face) the positive electrode **18** when incorporated into the lithium-sulfur battery **30**, **30'**.

[0024] The polycation(s) **16** penetrate into at least some of the pores of the porous polymer membrane **12** and/or the porous carbon coating **14**. As schematically illustrated in FIGS. **1** and **2**, the polycation(s) **16** may have a gradient distribution through the membrane **12** (FIG. **1**) and/or the coating **14** (FIG. **2**). By "gradient distribution", it is meant that the concentration of the polycation(s) **16** is the highest at an area of the porous polymer membrane **12** and/or the porous carbon coating **14** that faces or is to face the negative electrode **20**, and decreases across the porous polymer membrane **12** and/or the porous carbon coating **14** in the direction of an area that faces or is to face the positive electrode **18**. In the example shown in FIG. **1**, the gradient distribution (100→0) decreases moving from the surface **15** to the surface **13**. Similarly, in the example shown in FIG. **2**, the gradient distribution (100→0) decreases moving from the surface **13** to an exterior surface **17** of the porous carbon coating **14**. When the polycation(s) **16** are present in both the porous polymer membrane **12** and the porous carbon coating **14**, the gradient distribution may decrease moving from the surface **15** of the porous polymer membrane **12** to the exterior surface **17** of the porous carbon coating **14**.

[0025] The gradient distribution of the polycation(s) **16** may be formed during the formation of the porous carbon coating **14** on the porous polymer membrane **12**. This process will now be described.

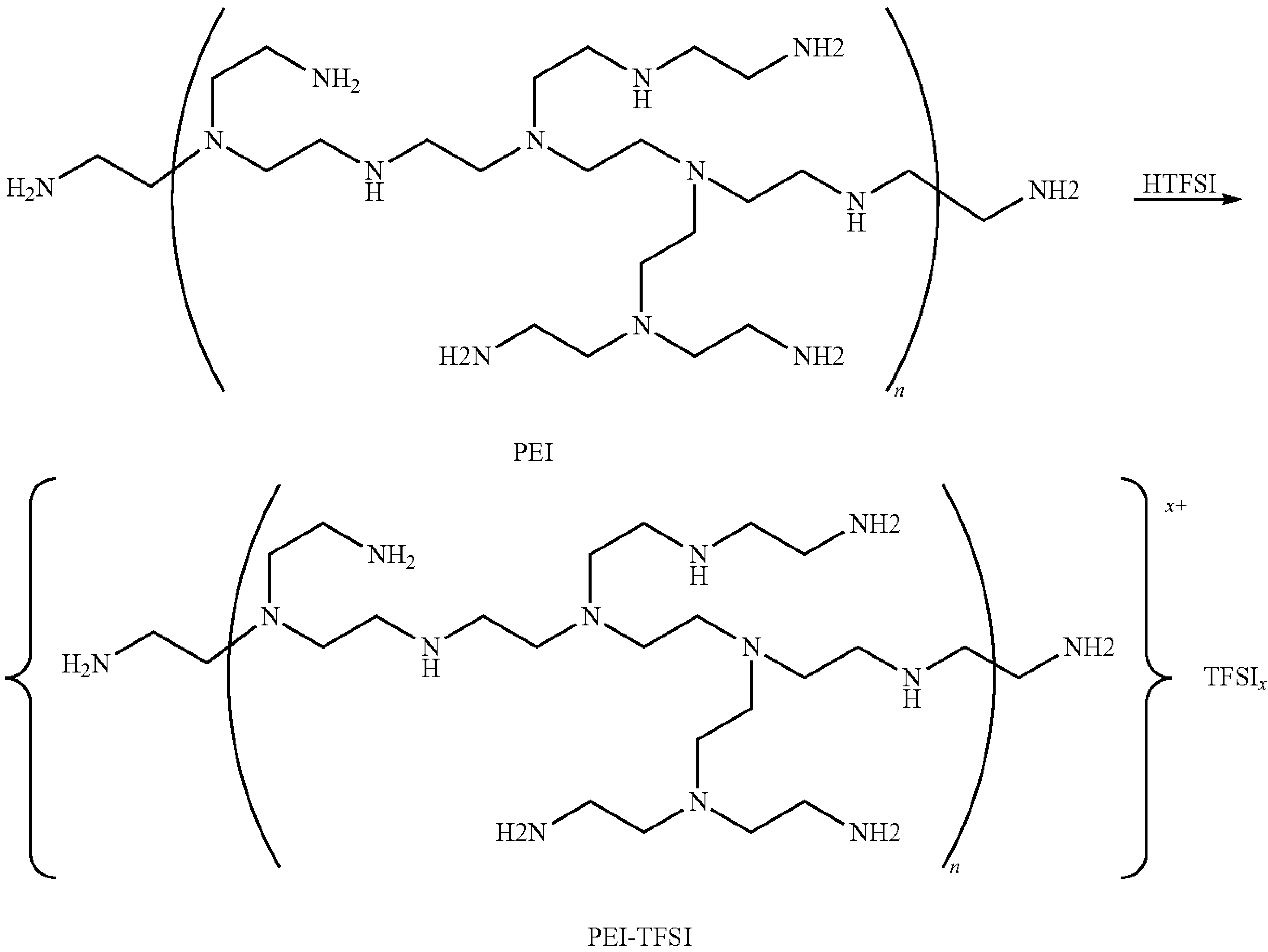
[0026] Both the gradient distribution of the polycation(s) **16** and the porous carbon coating **14** may be formed using a slurry. The slurry includes porous carbon particles and a polycation solution.

[0027] The porous carbon particles used in the slurry may be formed by exposing a carbon precursor to a predetermined temperature in an inert atmosphere (e.g., argon gas, nitrogen gas, etc.). This process carbonizes the carbon precursor to form the porous carbon particles having a pore volume ranging from about 5 cc/g to about 6 cc/g. In an example, porous carbon having a pore volume of about 5.68 cc/g is obtained using metal-organic framework-5 (MOF-5) as the carbon precursor and about 1000° C. as the predetermined temperature. As other examples, the carbon precursor may be Al-PCP (Al(OH)(1,4-naphthalenedicarboxylate) or ZIF-8 (Zn(2-methylimidazolate)2). In general, the carbonization temperature may range from about 800° C. to about 1200° C.

[0028] The porous carbon particles used in the slurry may also be commercially available carbons. Examples include activated carbon, such as AX-21 or XE-2, and mesoporous carbon, such as cmk-3 or cmk-8.

[0029] The polycation solution used in the slurry may include an organic solvent and the polycation(s) **16**. In one example, the polycation solution includes N-methyl-2-pyrrolidone (NMP) as the organic solvent, and polyethyleneimine-(trifluoromethane sulfonyl)imide (PEI-TFSI) as the polycation **16**. Other examples of the organic solvent include dimethylformamide (DMF), methanol, etc. It is to be understood, however, that the organic solvent selected may depend upon the solubility of the selected polycation. Other examples of the polycation **16** include poly(diallyldimethylammonium chloride) with the chlorine (Cl) replaced by TFSI or poly (acrylamide-co-diallyldimethylammonium chloride) (AMAC) with the chlorine (Cl) replaced by TFSI.

[0030] The polycation solution including NMP and PEI-TFSI may be formed by first titrating a polyethyleneimine (PEI) aqueous solution to a pH of 7 using a bis(trifluoromethane sulfonyl)imide (HTFSI) methanol solution. This forms the PEI-TFSI product in water and methanol. The reaction of PEI and HTFSI is shown below:



wherein $TFSI_x^-$ is a bis(trifluoromethyl sulfonyl)imide anion, x ranges from 100 to 100,000, and n ranges from 100 to 100,000. It is to be understood that the value of x depends upon the number average molecular weight of the polyethyleneimine that is used.

[0031] The water and methanol may be removed from the solution using a vacuum or evaporator. The liquid removal process leaves the PEI-TFSI product, which can be dissolved into the desired organic solvent. Generally, the amount of PEI-TFSI product to organic solvent renders a polycation solution having about 20 wt % of the polycation **16**.

[0032] To form the slurry, the porous carbon particles may be added to the polycation solution, or the polycation solution may be added to the porous carbon particles. In an example, the ratio of carbon to polycation solution in the slurry ranges from about 5% to about 50%.

[0033] The slurry may then be deposited on the porous polymer membrane **12** using any suitable technique. As examples, the slurry may be cast on the surface **13** of the porous polymer membrane **12**, or may be spread on the surface **13** of the porous polymer membrane **12**, or may be coated on the surface **13** of the porous polymer membrane **12** using a slot die coater.

[0034] The deposited slurry may then be exposed to a drying process. The drying process forms i) the porous carbon coating **14** on the surface **13**, and ii) the gradient distribution of the polycation(s) **16**. During drying, the polycation(s) **16** move to form the gradient. As such, the gradient distribution that is formed may depend, at least in part, on the drying rate. Generally, drying may take place at a temperature ranging from about 25° C. to about 65° C. for a time ranging from about 12 hours to about 48 hours. In an example, the drying process is carried out at about 25° C. for about 24 hours. In an example, the higher the temperature used during the drying process, the smaller the concentration gradient of the polycation(s) **16** will be from the porous carbon coating **14** to the polymer membrane **12**.

[0035] Whether the polycation(s) **16** penetrate the porous polymer membrane **12**, the porous carbon coating **14**, or both **12** and **14** depends, at least in part, upon the molecular size of the polycation(s) **16** and the size of the pores of the porous polymer membrane **12**.

[0036] When the pores of the porous polymer membrane **12** are larger than the molecular size of the polycation(s) **16**, the polycations **16** can penetrate into the membrane **12** during drying, as shown in FIG. **1**. If the drying process is performed at a low enough temperature and/or a long enough time and the polycations **16** are smaller than the pores of the membrane **12**, all of the polycation(s) **16** will migrate from the formed porous carbon coating **14** into the porous polymer membrane **12**. However, the drying process can be controlled so that polycation migration stops before all of the polycation(s) **16** are moved into the porous polymer membrane **12**. In these instances, the polycation gradient distribution may extend through at least part of the porous polymer membrane **12** and at least part of the porous carbon coating **14**. In an example, the molecular size of the polycation(s) **16** may be controlled by selecting a specific molecular weight of the polycation(s) **16**. Polycations **16** with a smaller molecular weight can move through a variety of membrane pore sizes, and allow the polycation(s) **16** to penetrate into the membrane **12** during drying, as shown in FIG. **1**.

[0037] When the pores of the porous polymer membrane **12** are smaller than the molecular size of the polycation(s) **16**, the polycations **16** cannot penetrate the membrane **12** during drying. In these instances, the polycation(s) **16** migrate toward the surface **13** of the porous polymer membrane **12** within the porous carbon coating **14**. This results in the gradient distribution forming in the porous carbon coating **14**, as shown in FIG. **2**. In an example, the gradient shown in FIG. **2** may be achieved by selecting a large molecular weight polycation(s) **16**, thereby preventing the polycation(s) **16** from penetrating the membrane **12** during drying.

[0038] When the polycation(s) **16** are located at or near the interface between the surface **13** of the porous polymer membrane **12** and the porous carbon coating **14**, the polycation(s) **16** can serve as a binder for the porous carbon coating **14**.

[0039] As illustrated in both FIGS. **1** and **2**, the separators **10**, **10'** are positioned between the positive electrode **18** and the negative electrode **20** so that the porous carbon coating **14** faces the positive electrode **18**. The separators **10**, **10'** respectively operate as an electrical insulator (preventing the occurrence of a short), a mechanical support, and a barrier to prevent physical contact between the two electrodes **18**, **20**. The separators **10**, **10'** also ensure passage of lithium ions (identified by the Li^+) through an electrolyte filling its pores. However, as discussed above, the separators **10**, **10'** also block the passage of polysulfide intermediates through absorption in the porous carbon coating **14**, soft acid-soft base interaction between the polycation **16** and polysulfide intermediates, and/or and the polycation(s) **16** filling at least some of the pores of the membrane **12** and/or coating **14**.

[0040] The positive electrode **18** of the lithium-sulfur battery **30**, **30'** may be formed from any sulfur-based active material that can sufficiently undergo lithium intercalation and deintercalation while functioning as the positive terminal of the battery **30**, **30'**. Examples of sulfur-based active materials include S_8, Li_2S_8, Li_2S_6, Li_2S_4, Li_2S_3, Li_2S_2, and Li_2S. Another example of the sulfur-based active material includes a sulfur-carbon composite. In an example, the weight ratio of S to C in the sulfur-carbon composite ranges from 1:9 to 8:1.

[0041] The positive electrode **18** may also include a polymer binder material to structurally hold the sulfur-based active material together. The polymer binder material may be made of at least one of polyvinylidene fluoride (PVdF), an ethylene propylene diene monomer (EPDM) rubber, carboxymethyl cellulose (CMC), styrene-butadiene rubber (SBR), styrene-butadiene rubber carboxymethyl cellulose (SBR-CMC), polyacrylic acid (PAA), cross-linked polyacrylic acid-polyethylenimine, polyvinyl alcohol (PVA), polyimide, poly(acrylamide-co-diallyl dimethyl ammonium chloride), polyethylene oxide (PEO), or sodium alginate or other water-soluble binders. Still further, the positive electrode **18** may include a conductive carbon material. In an example, the conductive carbon material is a high surface area carbon, such as acetylene black (i.e., carbon black). Other examples of suitable conductive fillers, which may be used alone or in combination with carbon black, include graphene, graphite, carbon nanotubes, and/or carbon nanofibers. One specific example of a combination of conductive fillers is carbon black and carbon nanofibers.

[0042] The positive electrode **18** may include from about 40% by weight to about 90% by weight (i.e., 90 wt %) of the sulfur-based active material. The positive electrode **18** may include from 0% by weight to about 30% by weight of the conductive filler. Additionally, the positive electrode **18** may include from 0% by weight to about 20% by weight of the polymer binder. In an example, the positive electrode **18**

includes about 85 wt % of the sulfur-based active material, about 10 wt % of the conductive carbon material, and about 5 wt % of the binder.

[0043] The negative electrode **20** of the lithium-sulfur battery **30**, **30'** may include any lithium host material **44** that can sufficiently undergo lithium plating and stripping while functioning as the negative terminal of the lithium-sulfur battery **30**, **30'**. Examples of the negative electrode lithium host material (i.e., active material) **44** include graphite or a low surface area amorphous carbon. Graphite is widely utilized as the lithium host material because it exhibits reversible lithium intercalation and deintercalation characteristics, is relatively non-reactive, and can store lithium in quantities that produce a relatively high energy density. Commercial forms of graphite that may be used to fabricate the negative electrode **20** are available from, for example, Timcal Graphite & Carbon (Bodio, Switzerland), Lonza Group (Basel, Switzerland), or Superior Graphite (Chicago, Ill.). Other materials can also be used to form the lithium host material **44** of the negative electrode **20**, such as, for example, lithium titanate, silicon or silicon-carbon composites, tin oxide, or lithiated silicon (e.g., $LiSi_x$). Porous silicon is shown as the lithium host material in FIGS. **1** and **2**.

[0044] The negative electrode **20** may also include a polymer binder material **48** to structurally hold the lithium host material together. Example binders include polyvinylidene fluoride (PVdF), an ethylene propylene diene monomer (EPDM) rubber, sodium alginate, styrene-butadiene rubber (SBR), styrene-butadiene rubber carboxymethyl cellulose (SBR-CMC), polyacrylic acid (PAA), cross-linked polyacrylic acid-polyethylenimine, polyvinyl alcohol (PVA), polyimide, poly(acrylamide-co-diallyl dimethyl ammonium chloride), polyethylene oxide (PEO), or carboxymethyl cellulose (CMC). These negative electrode materials may also be mixed with a high surface area carbon, such as acetylene black (i.e., carbon black) or another conductive filler **46**. Other examples of suitable conductive fillers **46**, which may be used alone or in combination with carbon black, include graphene, graphite, carbon nanotubes, and/or carbon nanofibers. One specific example of a combination of conductive fillers is carbon black and carbon nanofibers. The conductive filler **46** may be used to ensure electron conduction between the negative electrode lithium host material **44** and, for example, a negative-side current collector **20***a*.

[0045] As shown in FIGS. **1** and **2**, the lithium-sulfur battery **30**, **30'** may also include a positive-side current collector **18***a* and the previously mentioned negative-side current collector **20***a* positioned in contact with the positive electrode **18** and the negative electrode **20**, respectively, to collect and move free electrons to and from an external circuit **22**. The positive-side current collector **18***a* may be formed from aluminum or any other appropriate electrically conductive material known to skilled artisans. The negative-side current collector **20***a* may be formed from copper or any other appropriate electrically conductive material known to skilled artisans.

[0046] Each of the positive electrode **18**, the negative electrode **20**, and the separator **10**, **10'** is soaked in an electrolyte solution. Any appropriate electrolyte solution that can conduct lithium ions between the negative electrode **20** and the positive electrode **18** may be used in the lithium-sulfur battery **30**, **30'**. In one example, the non-aqueous electrolyte solution may be an ether based electrolyte that is stabilized with lithium nitrite. Other non-aqueous liquid electrolyte solutions may include a lithium salt dissolved in an organic solvent or a mixture of organic solvents. Examples of lithium salts that may be dissolved in the ether to form the non-aqueous liquid electrolyte solution include $LiClO_4$, $LiAlCl_4$, LiI, LiBr, $LiB(C_2O_4)_2$ (LiBOB), $LiBF_2(C_2O_4)$ (LiODFB), LiSCN, $LiBF_4$, $LiB(C_6H_5)_4$, $LiAsF_6$, $LiCF_3SO_3$, $LiN(FSO_2)_2$ (LIFSI), $LiN(CF_3SO_2)_2$ (LITFSI), $LiPF_6$, $LiPF_4(C_2O_4)$ (LiFOP), $LiNO_3$, and mixtures thereof. The ether based solvents may be composed of cyclic ethers, such as 1,3-dioxolane, tetrahydrofuran, 2-methyltetrahydrofuran, and chain structure ethers, such as 1,2-dimethoxyethane, 1-2-diethoxyethane, ethoxymethoxyethane, tetraethylene glycol dimethyl ether (TEGDME), polyethylene glycol dimethyl ether (PEGDME), and mixtures thereof.

[0047] The lithium-sulfur battery **30**, **30'** also includes the interruptible external circuit **22** that connects the positive electrode **18** and the negative electrode **20**. The lithium-sulfur battery **30**, **30'** may also support a load device **24** that can be operatively connected to the external circuit **22**. The load device **24** receives a feed of electrical energy from the electric current passing through the external circuit **22** when the lithium-sulfur battery **30**, **30'** is discharging. While the load device **24** may be any number of known electrically-powered devices, a few specific examples of a power-consuming load device include an electric motor for a hybrid vehicle or an all-electrical vehicle, a laptop computer, a cellular phone, and a cordless power tool. The load device **24** may also, however, be a power-generating apparatus that charges the lithium-sulfur battery **30**, **30'** for purposes of storing energy. For instance, the tendency of windmills and solar panels to variably and/or intermittently generate electricity often results in a need to store surplus energy for later use.

[0048] The lithium-sulfur battery **30**, **30'** can include a wide range of other components that, while not depicted here, are nonetheless known to skilled artisans. For instance, the lithium-sulfur battery **30**, **30'** may include a casing, gaskets, terminals, tabs, and any other desirable components or materials that may be situated between or around the positive electrode **18** and the negative electrode **20** for performance-related or other practical purposes. Moreover, the size and shape of the lithium-sulfur battery **30**, **30'**, as well as the design and chemical make-up of its main components, may vary depending on the particular application for which it is designed. Battery-powered automobiles and hand-held consumer electronic devices, for example, are two instances where the lithium-sulfur battery **30**, **30'** would most likely be designed to different size, capacity, and power-output specifications. The lithium-sulfur battery **30**, **30'** may also be connected in series and/or in parallel with other similar lithium-sulfur batteries **30**, **30'** to produce a greater voltage output and current (if arranged in parallel) or voltage (if arranged in series) if the load device **24** so requires.

[0049] The lithium-sulfur battery **30**, **30'** can generate a useful electric current during battery discharge (shown by reference numeral **26** in FIGS. **1** and **2**). During discharge, the chemical processes in the battery **30**, **30'** include lithium (Li^+) dissolution from the surface of the negative electrode **20** and incorporation of the lithium cations into alkali metal polysulfide salts (i.e., Li_2S_n, such as Li_2S_8, Li_2S_6, Li_2S_4, Li_2S_2, and Li_2S) in the positive electrode **18**. As such, polysulfides are formed (sulfur is reduced) within the positive electrode **18** in sequence while the battery **30**, **30'** is discharging. The chemical potential difference between the positive electrode **18** and the negative electrode **20** (ranging from approximately 1.5 to

3.0 volts, depending on the exact chemical make-up of the electrodes **18**, **20**) drives electrons produced by the dissolution of lithium at the negative electrode **20** through the external circuit **22** towards the positive electrode **18**. The resulting electric current passing through the external circuit **22** can be harnessed and directed through the load device **24** until the lithium in the negative electrode **20** is depleted and the capacity of the lithium-sulfur battery **30**, **30'** is diminished.

[0050] The lithium-sulfur battery **30**, **30'** can be charged or re-powered at any time by applying an external power source to the lithium-sulfur battery **30**, **30'** to reverse the electrochemical reactions that occur during battery discharge. During charging (shown at reference numeral **28** in FIGS. **1** and **2**), lithium plating to the negative electrode **20** takes place and sulfur formation within the positive electrode **18** takes place. The connection of an external power source to the lithium-sulfur battery **30**, **30'** compels the otherwise non-spontaneous oxidation of lithium at the positive electrode **18** to produce electrons and lithium ions. The electrons, which flow back towards the negative electrode **20** through the external circuit **22**, and the lithium ions (Li^+), which are carried by the electrolyte across the separator **10**, **10'** back towards the negative electrode **20**, reunite at the negative electrode **20** and replenish it with lithium for consumption during the next battery discharge cycle. The external power source that may be used to charge the lithium-sulfur battery **30**, **30'** may vary depending on the size, construction, and particular end-use of the lithium-sulfur battery **30**, **30'**. Some suitable external power sources include a battery charger plugged into an AC wall outlet and a motor vehicle alternator.

[0051] In FIGS. **3** and **4**, the lithium ion battery **40**, **40'** contains the negative electrode **20**, the negative side current collector **20***a*, a positive electrode **18'**, the positive-side current collector **18***a*, and the separator **10**, **10'** positioned between the negative electrode **20** and the positive electrode **18'**. It is to be understood that the separator **10** shown in FIG. **3** and the separator **10'** shown in FIG. **4** may be the same type of porous separators **10**, **10** that are described in reference to FIGS. **1** and **2**, respectively. In addition, the negative current collector **20***a* and positive current collector **18***a* described herein for the lithium-sulfur battery **30**, **30'** may also be used in the lithium ion battery **40**, **40'**.

[0052] As illustrated in both FIGS. **3** and **4**, the separators **10**, **10'** are positioned between the positive electrode **18'** and the negative electrode **20** so that the porous carbon coating **14** faces the positive electrode **18'**. The separators **10**, **10'** respectively operate as an electrical insulator (preventing the occurrence of a short), a mechanical support, and a barrier to prevent physical contact between the two electrodes **18'**, **20**. The separators **10**, **10'** also ensure passage of lithium ions (identified by the Li^+) through an electrolyte filling its pores. However, as discussed above, the separators **10**, **10'** include positively charged polycation(s) **16**, which may repel the positively charged transition metal cations, and thus may block the passage of the transition metal cations across the separators **10**, **10'**.

[0053] In FIGS. **3** and **4**, the positive electrode **18'** may be formed from any lithium-based active material **42** that can sufficiently undergo lithium insertion and deinsertion while aluminum or another suitable current collector is functioning as the positive terminal of the lithium ion battery **40**, **40'**. One common class of known lithium-based active materials **42** suitable for the positive electrode **18'** includes layered lithium transitional metal oxides. Some specific examples of the lithium-based active materials **42** include spinel lithium manganese oxide ($LiMn_2O_4$), lithium cobalt oxide ($LiCoO_2$), a nickel-manganese oxide spinel [$Li(Ni_{0.5}Mn_{1.5})O_2$], a layered nickel-manganese-cobalt oxide [$Li(Ni_xMn_yCo_z)O_2$ or $Li(Ni_xMn_yCo_z)O_4$, or a lithium iron polyanion oxide, such as lithium iron phosphate ($LiFePO_4$) or lithium iron fluorophosphate (Li_2FePO_4F). Other lithium-based active materials **42** may also be utilized, such as $LiNi_xM_{1-x}O_2$(M is composed of any ratio of Al, Co, and/or Mg), aluminum stabilized lithium manganese oxide spinel ($Li_xMn_{2-x}Al_yO_4$), lithium vanadium oxide (LiV_2O_5), Li_2MSiO_4 (M is composed of any ratio of Co, Fe, and/or Mn), xLi_2MnO_3-(1−x)$LiMO_2$ (M is composed of any ratio of Ni, Mn and/or Co), and any other high efficiency nickel-manganese-cobalt material. By "any ratio" it is meant that any element may be present in any amount. So, for example M could be Al, with or without Co and/or Mg, or any other combination of the listed elements.

[0054] The lithium-based active material **42** of the positive electrode **18'** may be intermingled with a polymeric binder and a conductive filler (e.g., high surface area carbon) (neither of which is shown). Any of the binders previously described for the negative electrode **20** of the lithium-sulfur battery **30**, **30'** may be used in the positive electrode **18'** of the lithium ion battery **40**, **40'**. The polymeric binder structurally holds the lithium-based active materials and the high surface area carbon together. An example of the high surface area carbon is acetylene black. The high surface area carbon ensures electron conduction between the positive-side current collector **18***a* and the active material particles of the positive electrode **18'**.

[0055] The negative electrode **20** of the lithium ion battery **40**, **40'** may include any lithium host material **44** that can sufficiently undergo lithium intercalation and deintercalation while copper or another suitable current collector **18***a* functions as the negative terminal of the lithium ion battery **40**, **40'**. Any of the lithium host materials (i.e., active materials) previously described for the negative electrode **20** of the lithium-sulfur battery **30**, **30'** may be used in the negative electrode **20** of the lithium ion battery **40**, **40'**. For example, the negative electrode lithium host material may be graphite or a silicon-based material. In FIGS. **3** and **4**, a porous silicon is shown as the lithium host material **33**.

[0056] The lithium-based active material of the negative electrode **20** may be intermingled with a polymeric binder **48** and a conductive filler **44** (e.g., high surface area carbon). Any of the binders previously described for the negative electrode **20** of the lithium-sulfur battery **30**, **30'** may be used in the negative electrode **20** of the lithium ion battery **40**, **40'**.

[0057] Any appropriate electrolyte solution that can conduct lithium ions between the negative electrode **20** and the positive electrode **18'** may be used in the lithium ion battery **40**, **40'**. Each of the positive electrode **18'**, the negative electrode **20**, and the separator **10**, **10'** is soaked in an electrolyte solution. In one example, the electrolyte solution may be a non-aqueous liquid electrolyte solution that includes a lithium salt dissolved in an organic solvent or a mixture of organic solvents. Examples of lithium salts that may be dissolved in an organic solvent to form the non-aqueous liquid electrolyte solution include $LiClO_4$, $LiAlCl_4$, LiI, LiBr, $LiB(C_2O_4)_2$ (LiBOB), $LiBF_2(C_2O_4)$ (LiODFB), LiSCN, $LiBF_4$, $LiB(C_6H_5)_4$, $LiAsF_6$, $LiCF_3SO_3$, $LiN(FSO_2)_2$ (LIFSI), $LiN(CF_3SO_2)_2$ (LITFSI), $LiPF_6$, $LiPF_4(C_2O_4)$ (LiFOP), $LiNO_3$, and mixtures thereof. Some examples of the organic based solvent may include cyclic carbonates (ethylene carbonate, propylene carbonate, butylene carbonate, fluoroethylene carbonate), linear carbonates (dimethyl carbonate, diethyl carbonate, ethylmethyl carbonate), aliphatic carboxylic esters (methyl formate, methyl acetate, methyl propionate), γ-lactones (γ-butyrolactone, γ-valerolactone), chain structure ethers (1,2-dimethoxyethane, 1-2-diethoxyethane, ethoxymethoxyethane, tetraglyme), cyclic ethers (tetrahydrofuran, 2-methyltetrahydrofuran, 1,3-dioxolane), and mixtures thereof.

[0058] As shown in FIGS. **3** and **4**, the lithium ion battery **40**, **40'** also includes an interruptible external circuit **22** that connects the negative electrode **20** and the positive electrode **18'**. The lithium ion battery **40**, **40'** may also support a load device **24** that can be operatively connected to the external circuit **22**. The load device **24** receives a feed of electrical energy from the electric current passing through the external circuit **22** when the lithium ion battery **40**, **40'** is discharging. While the load device **24** may be any number of known electrically-powered devices, a few specific examples of a power-consuming load device **24** include an electric motor for a hybrid vehicle or an all-electrical vehicle, a laptop computer, a cellular phone, and a cordless power tool. The load device **24** may also, however, be an electrical power-generating apparatus that charges the lithium ion battery **40**, **40'** for purposes of storing energy. For instance, the tendency of windmills and solar panels to variably and/or intermittently generate electricity often results in a need to store surplus energy for later use.

[0059] The lithium ion battery **40**, **40'** may also include a wide range of other components that, while not depicted here, are nonetheless known to skilled artisans. For instance, the lithium ion battery **40**, **40'** may include a casing, gaskets, terminals, tabs, and any other desirable components or materials that may be situated between or around the negative electrode **20** and the positive electrode **18'** for performance-related or other practical purposes. Moreover, the size and shape of the lithium ion battery **40**, **40'**, as well as the design and chemical make-up of its main components, may vary depending on the particular application for which it is designed. Battery-powered automobiles and hand-held consumer electronic devices, for example, are two instances where the lithium ion battery **40**, **40'** would most likely be designed to different size, capacity, and power-output specifications. The lithium ion battery **40**, **40'** may also be connected in series and/or in parallel with other similar lithium ion batteries to produce a greater voltage output and current (if arranged in parallel) or voltage (if arranged in series) if the load device **24** so requires.

[0060] The lithium ion battery **40**, **40'** generally operates by reversibly passing lithium ions between the negative electrode **20** and the positive electrode **18'**. In the fully charged state, the voltage of the battery **40**, **40'** is at a maximum (typically in the range 2.0V to 5.0V); while in the fully discharged state, the voltage of the battery **40**, **40'** is at a minimum (typically in the range 0V to 2.0V). Essentially, the Fermi energy levels of the active materials in the positive and negative electrodes **18'**, **20** change during battery operation, and so does the difference between the two, known as the battery voltage. The battery voltage decreases during discharge, with the Fermi levels getting closer to each other. During charge, the reverse process is occurring, with the battery voltage increasing as the Fermi levels are being driven apart. During battery discharge, the external load device **24** enables an electronic current flow in the external circuit **22** with a direction such that the difference between the Fermi levels (and, correspondingly, the cell voltage) decreases. The reverse happens during battery charging: the battery charger forces an electronic current flow in the external circuit **22** with a direction such that the difference between the Fermi levels (and, correspondingly, the cell voltage) increases.

[0061] At the beginning of a discharge, the negative electrode **20** of the lithium ion battery **40**, **40'** contains a high concentration of intercalated lithium while the positive electrode **18'** is relatively depleted. When the negative electrode **20** contains a sufficiently higher relative quantity of intercalated lithium, the lithium ion battery **40**, **40'** can generate a beneficial electric current by way of reversible electrochemical reactions that occur when the external circuit **24** is closed to connect the negative electrode **20** and the positive electrode **18'**. The establishment of the closed external circuit under such circumstances causes the extraction of intercalated lithium from the negative electrode **20**. The extracted lithium atoms are split into lithium ions (identified by the black dots) and electrons (e^-) as they leave an intercalation host at the negative electrode-electrolyte interface.

[0062] The chemical potential difference between the positive electrode **18'** and the negative electrode **20** (ranging from about 2.0V to about 5.0V, depending on the exact chemical make-up of the electrodes **20**, **18'**) drives the electrons (e^-) produced by the oxidation of intercalated lithium at the negative electrode **20** through the external circuit **22** towards the positive electrode **18'**. The lithium ions are concurrently carried by the electrolyte solution through the porous separator **10**, **10'** towards the positive electrode **18'**. The electrons (e^-) flowing through the external circuit **22** and the lithium ions migrating across the porous separator **10**, **10'** in the electrolyte solution eventually reconcile and form intercalated lithium at the positive electrode **18'**. The electric current passing through the external circuit **22** can be harnessed and directed through the load device **24** until the level of intercalated lithium in the negative electrode **20** falls below a workable level or the need for electrical energy ceases.

[0063] The lithium ion battery **40**, **40'** may be recharged after a partial or full discharge of its available capacity. To charge the lithium ion battery **40**, **40'** an external battery charger is connected to the positive and the negative electrodes **18'**, **20** to drive the reverse of battery discharge electrochemical reactions. During recharging, the electrons (e^-) flow back towards the negative electrode **20** through the external circuit **22**, and the lithium ions are carried by the electrolyte across the porous separator **10**, **10'** back towards the negative electrode **20**. The electrons (e^-) and the lithium ions are reunited at the negative electrode **20**, thus replenishing it with intercalated lithium for consumption during the next battery discharge cycle.

[0064] The external battery charger that may be used to charge the lithium ion battery **40**, **40'** may vary depending on the size, construction, and particular end-use of the lithium ion battery **40**, **40'**. Some suitable external battery chargers include a battery charger plugged into an AC wall outlet and a motor vehicle alternator.

[0065] Examples of the batteries **30**, **30'**, **40**, **40'** may be used in a variety of different applications. For example the batteries **30**, **30'**, **40**, **40'** may be used in different devices, such as a battery operated or hybrid vehicle, a laptop computer, a cellular phone, a cordless power tool, or the like.

[0066] To further illustrate the present disclosure, an example is given herein. It is to be understood that this example is provided for illustrative purposes and is not to be construed as limiting the scope of the disclosed example(s).

Example

[0067] A separator was prepared with a porous carbon coating and a gradient distribution of PEI-TFSI.

[0068] A 10 wt % polyethyleneimine aqueous solution was titrated to a pH of 7 using a 10 wt % bis-(trifluoromethane sulfonyl)imide methanol solution. The PEI-TFSI product was obtained after removing water and methanol though vacuum. The PEI-TFSI product was dissolved into NMP so that a polycation solution with 20 wt % PEI-TFSI was obtained.

[0069] Porous carbon with a pore volume of 5.68 cc/g was obtained by heating MOF-5 at 1000° C. in argon.

[0070] A slurry was prepared by mixing the porous carbon with the polycation solution. This slurry was cast on a polypropylene membrane (CELGARD 2500) and was dried at room temperature (~25° C.) for about 24 hours. This formed the example separator.

[0071] Two comparative porous separators were also used. The first comparative porous separator was an unmodified polypropylene separator (CELGARD 2500).

[0072] The second comparative separator was made with a coating of some of the porous carbon described above and polyvinylidene fluoride on a polypropylene separator (CELGARD 2500). More particularly, the second comparative separator was prepared by mixing 20 mg of the porous carbon with 80 mg of PVDF. 200 mg of NMP was added to make a slurry (or suspension) under magnetic stirring for about 12 hours. The slurry was then cast onto the separator (CELGARD 2500). Finally, the second comparative separator was obtained by drying at 25° C. for about 24 hours.

[0073] The first comparative example separator (1), the second comparative example separator (2), and the example separator (3) were each evaluated using half cells. Within the half cells, the first comparative example separator (1), the second comparative example separator (2), and the example separator (3) were paired with a sulfur positive electrode having a sulfur loading of 1.85 g/cm^2 in 0.6 M LiNO$_3$ plus 0.4 M LiTFSI in dimethoxyethane:1,3-dioxolane (DME:DIOX) 1:1). The galvanostatic cycling performance of the first comparative example separator (1), the second comparative example separator (2), and the example separator (3) was tested by cycling between 1.7V and 2.75V at a rate of C/10 at room temperature for up to 60 cycles.

[0074] The cycling performance and Coulombic efficiency results are shown in FIG. **5**. In particular, the capacity (mAh/g$_s$) is shown on the left Y-axis (labeled "C"), the Coulombic efficiency (%) is shown on the right Y-axis (labeled "%"), and the cycle number is shown on the X-axis (labeled "#"). As noted above, "1" represents the results for the half cell with the first comparative example separator, "2" represents the results for the half cell with the second comparative example separator, and "3" represents the results for the half cell with the example separator. Both the example separator and the second comparative separator (which did include a carbon/polymer coating) improved in capacity and Coulombic efficiency compared to the first comparative example (i.e., the uncoated separator). The capacity results for the example separator were much better than both the first and second comparative electrodes. The Coulombic efficiency for the example separator was much better than the first comparative electrode, and was comparable to the second comparative electrode. Overall, the example separator exhibited the best performance, which may have been due, at least in part, to the soft acid (ammonium)-base (polysulfide) interaction.

[0075] FIG. **6** illustrates the voltage profile of the three half cells in the 2nd cycle. In FIG. **6**, the voltage (V) is shown on the Y-axis (labeled "V") and the specific capacity (mAh/g$_s$) is shown on the X-axis (labeled "C"). As shown in FIG. **6**, the introduction of the polycations maintains the plateau voltage and improved the utilization of the sulfur based active materials. This results in a higher energy density.

[0076] A backscatter electron image of the second comparative example was taken and is shown in FIG. **7**A. As illustrated, the second comparative example included the CELGARD 2500 membrane (labeled **12**) and the carbon/PVDF coating (labeled **14'**). In this comparative example, PVDF is the only source of F, and thus the gradient formed in this comparative example can be readily seen through elemental mapping (FIG. **7**B). In the example separator, the N signal is very weak from PEI-TFSI. As a result, it is difficult to obtain a similar elemental mapping of F for the example separator. It is believed that the example separator has a similar polycation gradient as the second comparative example, at least in part because the same solvent (i.e., NMP) and drying conditions were used.

[0077] It is to be understood that the ranges provided herein include the stated range and any value or sub-range within the stated range. For example, a range of from 100 to 100,000 should be interpreted to include not only the explicitly recited limits of 100 to 100,000, but also to include individual values, such as 225, 3,000, 50,050, etc., and sub-ranges, such as from 500 to about 75,000; from 1,100 to 95,000, etc. Furthermore, when "about" is utilized to describe a value, this is meant to encompass minor variations (up to +/−5%) from the stated value.

[0078] Reference throughout the specification to "one example", "another example", "an example", and so forth, means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the example is included in at least one example described herein, and may or may not be present in other examples. In addition, it is to be understood that the described elements for any example may be combined in any suitable manner in the various examples unless the context clearly dictates otherwise.

[0079] In describing and claiming the examples disclosed herein, the singular forms "a", "an", and "the" include plural referents unless the context clearly dictates otherwise.

[0080] While several examples have been described in detail, it is to be understood that the disclosed examples may be modified. Therefore, the foregoing description is to be considered non-limiting.

What is claimed is:

1. A lithium-based battery separator, comprising:

a porous polymer membrane having opposed surfaces;

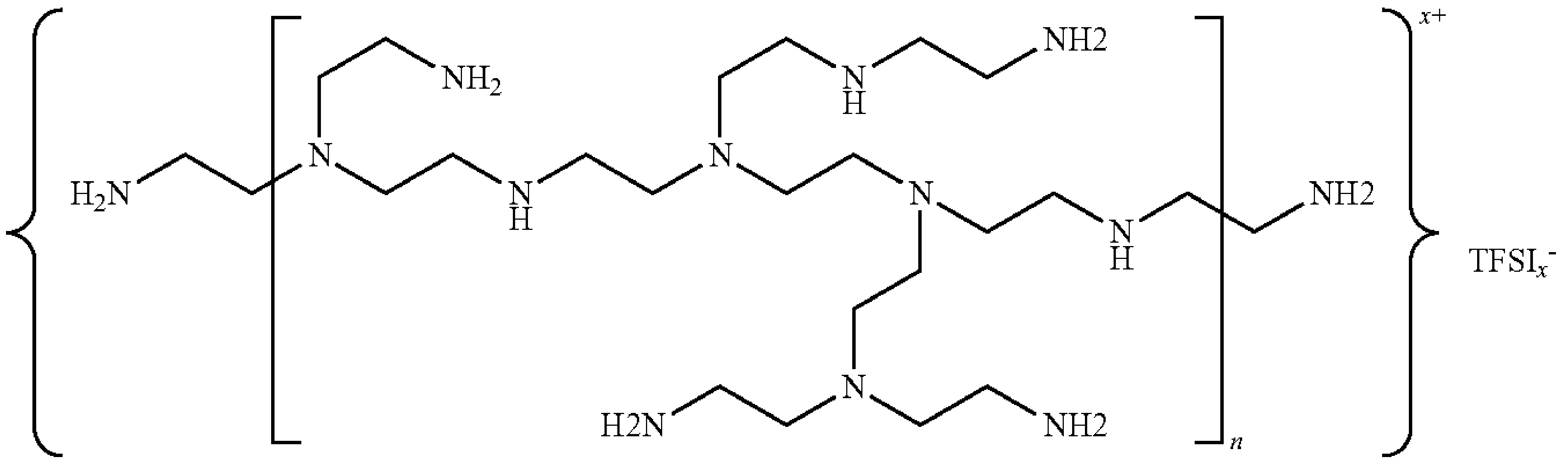
a porous carbon coating formed on one of the opposed surfaces of the porous polymer membrane; and

polycations incorporated in the porous carbon coating, in the porous polymer membrane, or in both the porous carbon coating and the porous polymer membrane.

2. The lithium-based battery separator as defined in claim **1** wherein the polycations are incorporated in the porous polymer membrane and have a gradient distribution that increases towards an other of the opposed surfaces of the porous polymer membrane.

3. The lithium-based battery separator as defined in claim **1** wherein the polycations are incorporated in the porous carbon coating and have a gradient distribution that increases towards the one of the opposed surfaces of the porous polymer membrane.

4. The lithium-based battery separator as defined in claim **1** wherein the polycations have the following structure:



wherein TFSI$_x^-$ is a bis(trifluoromethyl sulfonyl)imide anion, x ranges from 100 to 100,000, and n ranges from 100 to 100,000.

5. A method for manufacturing a lithium-based battery separator, the method comprising:

casting a slurry on one of two opposed surfaces of a porous polymer membrane, the slurry including porous carbon particles and polycations; and

exposing the cast slurry to a drying process, thereby forming i) a porous carbon coating on the one of the two opposed surfaces of the porous polymer membrane, and ii) a gradient distribution of the polycations in the porous carbon coating, in the porous polymer membrane, or in both the porous carbon coating and the porous polymer membrane.

6. The method as defined in claim **5** wherein prior to casting the slurry, the method further comprises making a polycation solution and adding the porous carbon particles to the polycation solution.

7. The method as defined in claim **6**, further comprising making the polycation solution by:

titrating a polyethyleneimine aqueous solution to a pH of 7 using a bis(trifluoromethane sulfonyl)imide methanol solution, thereby forming a polycation product in water and methanol;

removing the water and methanol; and

dissolving the polycation product in an organic solvent.

8. The method as defined in claim **6**, further comprising making the porous carbon particles by exposing a carbon precursor to a predetermined temperature in an inert atmosphere thereby carbonizing the carbon precursor.

9. The method as defined in claim **8** wherein the carbon precursor is metal-organic framework-5 (MOF-5).

10. The method as defined in claim **6** wherein the drying process is performed at about 25° C. for about 24 hours.

11. A lithium-based battery, comprising:

a negative electrode;

a positive electrode including an active material;

a separator positioned between the negative electrode and the positive electrode, the separator including:

a porous polymer membrane having opposed surfaces, one of the opposed surfaces facing the positive electrode;

a porous carbon coating formed on the one of the opposed surfaces; and

polycations incorporated in the porous carbon coating, in the porous polymer membrane, or in both the porous carbon coating and in the porous polymer membrane; and

an electrolyte solution soaking each of the positive electrode, the negative electrode, and the separator.

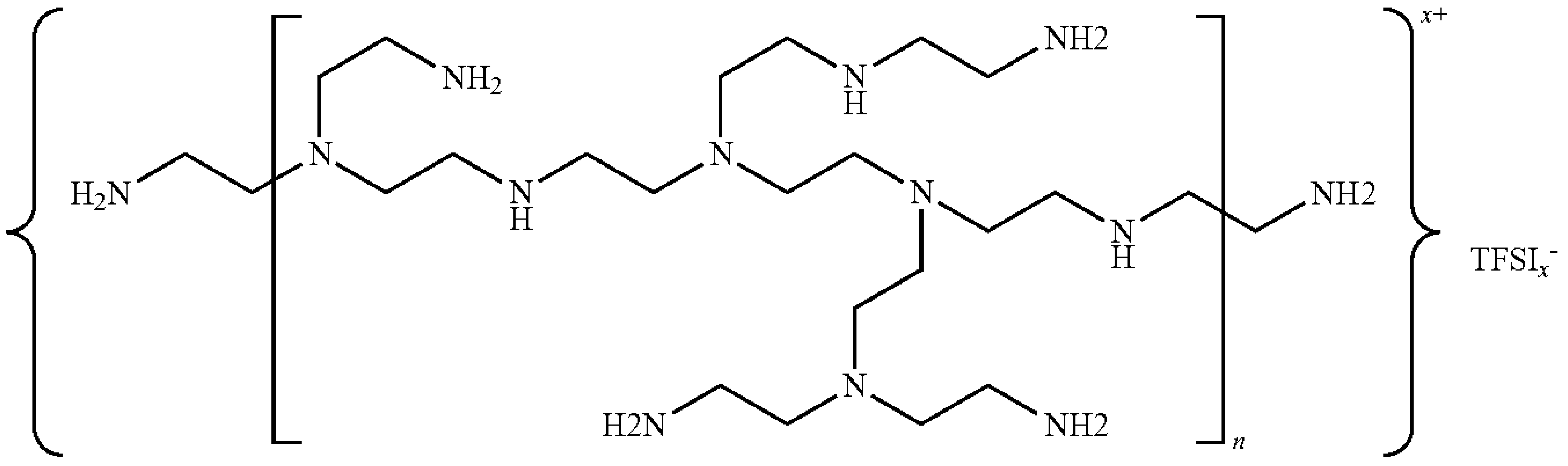
12. The lithium-based battery as defined in claim **11** wherein the lithium-based battery is a lithium-sulfur battery.

13. The lithium-based battery as defined in claim **11** wherein the lithium-based battery is a lithium ion battery.

14. The lithium-based battery as defined in claim **11** wherein the polycations are incorporated in the porous polymer membrane and have a gradient distribution that increases towards an other of the opposed surfaces of the porous polymer membrane.

15. The lithium-based battery as defined in claim **11** wherein the polycations are incorporated in the porous carbon coating and have a gradient distribution that increases towards the one of the opposed surfaces of the porous polymer membrane.

16. The lithium-based battery as defined in claim **11** wherein the polycations have the following structure:



wherein $TFSI_x^-$ is a bis(trifluoromethyl sulfonyl)imide anion, x ranges from 100 to 100,000, and n ranges from 100 to 100,000.

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